

German Patent No. 274357

Job No.: 493-112876

Ref.: Ref. No. TE422874

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GERMAN PATENT OFFICE

PATENT NO.: 274357

(Patent Specification)

German Cl.: 22b, Group 2

Issued Date: May 18, 1914

Patented in Germany with effect from: June 2, 1911

PROCESS FOR THE SYNTHESIS OF DIANTHRAQUINONYL THIOETHERS

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Anthraquinone mercaptan anthraquinonyl ethers have not previously been known. The methods that lead to the synthesis of anthraquinone mercaptan aryl ethers and anthraquinone mercaptan alkyl ethers - whereby these methods have respectively been described in [German] patent specifications 116951, Class 12 and 224589, Class 22 and which comprise the heating of negatively substituted anthraquinone derivatives with aromatic mercaptans and aliphatic mercaptans, respectively - fail in the case of using anthraquinone mercaptans because evidently, an extraneous action of the alcoholic or aqueous alkali on the halogenoanthraquinones takes place at the temperature that is required for the reaction.

It has now been found that dianthraquinonyl thioethers are obtained in pure form and in good yields if halogenoanthraquinones are heated in a high-boiling, inert solvent - with or without the addition of a catalyst, such as, e.g., copper or its salts - with the alkali metal salts of anthraquinone mercaptans. Instead of the ready-made alkali metal salts of the mercaptan, use can also be made of the free mercaptan together with acid-binding agents, such as the alkali metal carbonates, acetates, etc.

The dianthraquinonyl thioethers form valuable vat dyes and they can also serve as starting materials for the synthesis of other dyes.

Example 1

11 parts of the sodium salt of anthraquinone-2-mercaptan and 10 parts of 1-chloroanthraquinone are introduced into 100 parts of molten naphthalene and - following the addition of 0.2 part cuprous chloride - boiled until an increase in the formation of the condensation product in the melt can no longer be perceived. The 1,2'-dianthraquinonyl thioether, in the form of a yellow crystalline powder, is obtained from the melt after adding pyridine, whereby the melt had been cooled to approximately 100°C. Its solution in organic solvents is yellow; its solution in fuming sulfuric acid (20 percent) is green; its solution in sulfuric acid monohydrate is blue; and its solution in sulfuric acid of 66° Bé strength is gray-blue. Upon diluting with water, the latter initially becomes brownish-purple, and then the dye separates in the form of yellow flakes that dissolve in alkaline hydrosulfite to give an orange-red dyeing liquor with which sulfur-yellow colored dyeing effects are obtained on cotton.

If the sodium salt of anthraquinone-2-mercaptan is replaced by the sodium salt of anthraquinone-1-mercaptan, then 1,1'-dianthraquinonyl thioether is obtained in the form of an orange-brown crystalline powder whose solutions in pyridine are orange and whose solutions in fuming sulfuric acid of 20 percent concentration are emerald green, and whose solutions in concentrated sulfuric acid are olive green. Its dyeing effects that are produced in the dyeing liquor are red-tinged yellow.

Example 2

10 parts of anthraquinone-2-mercaptan, 15 parts of 1-benzoylamino-4-chloroanthraquinone, 10 parts of powdered potassium carbonate, 0.1 part copper bronze, and 100 parts of naphthalene are boiled for 8 h. 1-benzoylamino-4,2'-dianthraquinonyl thioether, in the form of scarlet red needles, is obtained from the melt that was worked up as in Example 1, whereby these needles give a yellow-red solution in pyridine and a green solution in concentrated sulfuric acid. Vivid yellow-red dyeing effects of great fastness are obtained in the dyeing liquor.

Example 3

10 parts of anthraquinone-2-mercaptan, 15 parts of 4-bromo-1-methylanthrapyridone, 10 parts of dehydrated sodium acetate, and 100 parts of nitrobenzene are heated at the boiling point of the latter for approximately 6 h. The condensation product separates from the melt and has the form of orange-colored needles. Its solution in concentrated sulfuric acid is blue-tinged red and the finished dyeing effects on cotton are orange-yellow.

The anthraquinone dimercaptans and the substitution products of the anthraquinone mercaptans or those of the halogenoanthraquinones behave completely analogously. Thus a

brownish-purple vat dye is obtained from, e.g., anthraquinone-1,5-dimercaptan + 2 mol of 1-chloro-4-oxyanthraquinone, and an orange-yellow wool dye is obtained from 1-chloroanthraquinonesulfonic acid + anthraquinone-1-mercaptan. The properties of some of the dyes that are prepared in this way are contained in the following table:

20	Thioäther aus (1)	(2) Aussehen	(3) Lösung in konz. H_2SO_4	(4) Färbung auf Baumwolle	80
25	(5) Anthrachinon-2-merkaptan + 1-Chloranthrachinon	(6) gelbe quadratische Blättchen	(7) graublau	(8) schwefelgelb	85
30	(9) Anthrachinon-2-merkaptan + 2-Chloranthrachinon	(10) orangegelbe Nadeln	(11) rotviolett	(12) goldgelb	90
35	(13) Anthrachinon-1-merkaptan + 1-Chloranthrachinon	(14) orangebraune Kristalle	(15) olivgrün	(16) rotstichig gelb	95
40	(17) Anthrachinon-2-merkaptan + 1-Benzoylamino-4-chlor-A	(18) scharlachrote Nadeln	(19) grün	(20) scharlachrot	100
45	(21) Anthrachinon-2-merkaptan + 4-Brom-1-N-methylantrapyridon	(22) orange Nadeln	(23) bläustichig rot	(24) orangegelb	105
50	(25) Anthrachinon-1·5-dimercaptan + 2 Mol. 1-Chlor-4-oxyanthrachinon	(26) dunkelblaues Pulver (Alkalisalz)	(19) grün	(27) braunrot	110
55	(28) Anthrachinon-2-merkaptan (2 Mol.) + 1·5-Dichloranthrachinon	(29) orangegelbe Nadeln	(30) sehr schwer löslich, blau	(12) goldgelb	115
60	(31) Anthrachinon-2-merkaptan (2 Mol.) + 1·8-Dichloranthrachinon	(22) orange Nadeln	(7) graublau	(24) orangegelb	120
	(32) Anthrachinon-2-merkaptan (2 Mol.) + 1·4-Dichloranthrachinon	(33) scharlachrote Prismen	(34) stumpfgrün	(35) orange	
	(36) Anthrachinon-2-merkaptan (2 Mol.) + 2·7-Dichloranthrachinon	(37) gelbes Pulver	(38) bläuviolett	(12) goldgelb	
	(39) Anthrachinon-2-merkaptan (4 Mol.) + 1·4·5·8-Tetrachloranthrachinon	(40) rote Nadeln	(7) graublau	(41) gelb	
	(42) Anthrachinon-1-merkaptan + 1-Chloranthrachinon-5-sulfosäure	(43) orangefarbenes Pulver	(15) olivgrün	auf Wolle sauer gefärbt, orangegelb	

- Key:
- 1 Thioether from
 - 2 Appearance
 - 3 Solution in concentrated H_2SO_4
 - 4 Dyeing effect on cotton
 - 5 Anthraquinone-2-mercaptan + 1-chloroanthraquinone
 - 6 Yellow, square leaflets

- 7 Gray-blue
- 8 Sulfur-colored yellow
- 9 Anthraquinone-2-mercaptan + 2-chloroanthraquinone
- 10 Orange-yellow needles
- 11 Red-violet
- 12 Gold-colored
- 13 Anthraquinone-1-mercaptan + 1-chloroanthraquinone
- 14 Orange-brown crystals
- 15 Olive green
- 16 Red-tinged yellow
- 17 Anthraquinone-2-mercaptan + 1-benzoylamino-4-chloro-A [sic;
1-benzoylamino-4-chloroanthraquinone]
- 18 Scarlet red needles
- 19 Green
- 20 Scarlet red
- 21 Anthraquinone-2-mercaptan + 4-bromo-1-N-methylanthrapyridone
- 22 Orange needles
- 23 Blue-tinged red
- 24 Orange-yellow
- 25 Anthraquinone-1,5-dimercaptan + 2 moles of 1-chloro-4-oxyanthraquinone
- 26 Dark-blue powder (alkali metal salt)
- 27 Brownish-purple
- 28 Anthraquinone-2-mercaptan (2 moles) + 1,5-dichloroanthraquinone
- 29 Orange-yellow needles
- 30 Very sparingly soluble, blue
- 31 Anthraquinone-2-mercaptan (2 mol) + 1,8-dichloroanthraquinone
- 32 Anthraquinone-2-mercaptan (2 mol) + 1,4-dichloroanthraquinone
- 33 Scarlet red prisms
- 34 Dull green
- 35 Orange
- 36 Anthraquinone-2-mercaptan (2 mol) + 2,7-dichloroanthraquinone
- 37 Yellow powder
- 38 Blue-violet
- 39 Anthraquinone-2-mercaptan (4 mol) + 1,4,5,8-tetrachloroanthraquinone
- 40 Red needles
- 41 Yellow
- 42 Anthraquinone-1-mercaptan + 1-chloroanthraquinone-5-sulfonic acid
- 43 Orange-colored powder
- 44 Orange-yellow on wool, acid dyed

Claim

Process for the synthesis of dianthraquinonyl thioethers comprising the feature that halogenoanthraquinones are heated in inert, high-boiling solvents - with or without the addition

of a catalyst - with free anthraquinone mercaptans in the presence of acid-binding agents, or with anthraquinone mercaptan salts.